EDGEWOOD CHEMICAL BIOLOGICAL CENTER
U.S. ARMY RESEARCH, DEVELOPMENT AND ENGINEERING COMMAND
Aberdeen Proving Ground, MD 21010-5424

ECBC-TR-1142

# SCREENING SAMPLES FOR ARSENIC BY INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY FOR TREATY SAMPLES

**Kristin K. Clark**
**Lynn D. Hoffland**

**RESEARCH AND TECHNOLOGY DIRECTORATE**

**February 2014**

Disclaimer

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorizing documents.

# REPORT DOCUMENTATION PAGE

*Form Approved*
*OMB No. 0704-0188*



| **1. REPORT DATE** *(DD-MM-YYYY)* | **2. REPORT TYPE** | **3. DATES COVERED** *(From - To)* |
|---|---|---|
| XX-02-2014 | Final | Aug 2012 - Oct 2012 |

**4. TITLE AND SUBTITLE**
Screening Samples for Arsenic by Inductively Coupled Plasma-Mass Spectrometry for Treaty Samples

**5a. CONTRACT NUMBER**

**5b. GRANT NUMBER**

**5c. PROGRAM ELEMENT NUMBER**

**6. AUTHOR(S)**
Clark, Kristin K.; and Hoffland, Lynn D.

**5d. PROJECT NUMBER**

**5e. TASK NUMBER**

**5f. WORK UNIT NUMBER**

**7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)**
Director, ECBC, ATTN: RDCB-DRC-F, APG, MD 21010-5424

**8. PERFORMING ORGANIZATION REPORT NUMBER**
ECBC-TR-1142

**9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)**
Organization for the Prohibition of Chemical Weapons
Mr. Hugh Gregg, Head OPCW Laboratory
Heulweg 28-30, 2288 GN Rijswijk The Netherlands

**10. SPONSOR/MONITOR'S ACRONYM(S)**
OPCW

**11. SPONSOR/MONITOR'S REPORT NUMBER(S)**

**12. DISTRIBUTION / AVAILABILITY STATEMENT**
Approved for public release; distribution unlimited.

**13. SUPPLEMENTARY NOTES**

**14. ABSTRACT:**
Arsenic is a metal found in chemical warfare agents (CWA), lewisite, and the hydrolysis products chlorovinyl arsonous acid (CVAA). One of the missions of the Forensic Analytical Center is to screen samples for compliance with the international treaty to not proliferate CWAs. In order to determine if a sample may contain a CWA screening techniques need to be established and validated. This report describes the screening method used for potential arsenic containing samples when an organic solvent may be present to mask the arsenic.

**15. SUBJECT TERMS**
Chlorovinylarsonous acid | Arsenic | OPCW
Dichloromethane interference | Lewisite | Hexane interference
Inductively coupled plasma- mass spectrometery

| **16. SECURITY CLASSIFICATION OF:** | | | **17. LIMITATION OF ABSTRACT** | **18. NUMBER OF PAGES** | **19a. NAME OF RESPONSIBLE PERSON** |
|---|---|---|---|---|---|
| | | | | | Renu B. Rastogi |
| **a. REPORT** | **b. ABSTRACT** | **c. THIS PAGE** | | | **19b. TELEPHONE NUMBER** *(include area code)* |
| U | U | U | UU | 32 | (410) 436-7545 |

Blank

# PREFACE

The work described in this report was started in August 2012 and completed in October 2012.

The use of either trade or manufacturers' names in this report does not constitute an official endorsement of any commercial products. This report may not be cited for purposes of advertisement.

This report has been approved for public release.

Blank

CONTENTS

FIGURES



TABLES

# SCREENING SAMPLES FOR ARSENIC BY INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY FOR TREATY SAMPLES

## 1. INTRODUCTION

The U.S. Army Edgewood Chemical Biological Center-Forensic Analytical Center (ECBC-FAC) is a designated lab under the Organization for the Prohibition of Chemical Weapons (OPCW). This organization is designed to implement the Chemical Weapons Convention treaty[1]. Independent experts comprise the Scientific Advisory Board, which is charged with the task of maintaining current technologies, methodologies and equipment to address relevant expertise and analysis for reports under the OPCW treaty. ECBC-FAC has participated in the generation of methods for the official Blue Book of *Recommended Operating Procedures for Analysis in the Verification of Chemical Disarmament*[2].

As part of the evaluation and actual screening process ECBC-FAC developed a new method to determine if chemical warfare agents (CWAs) containing arsenic are present. Arsenic is found in Arsenic trichloride, and the following chemical warfare agents and their degradation products: 1, 2-Chlorovinyldichloroarsine (Lewisite, L); Bis(2-chlorovinyl)chloroarsine (Lewisite 2, L-2); and Tris(2-chlorovinyl)arsine (Lewisite 3, L-3). L-2 and L-3 are often found as impurities in L-1.

Past tests and samples included interferents to make the analysis and positive identification of the compound(s) more challenging and realistic. The main interferents utilized in screening for L were the solvents used to dissolve the solid agents. Hexane and dichloromethane readily accompanied L in commercial formulations and test samples received for proficiency testing. The 6$^{th}$, 9$^{th}$, 21$^{st}$, 25$^{th}$, and 31$^{st}$ Official OPCW Proficiency Tests all contained arsenic-containing L-spiking chemicals. The hydrolyzed products, for example, chlorovinylarsonous acid (CVAA), are also important compounds to screen for in these samples, as they could indicate that L had been present.

### 1.1 Testing Requirements for OPCW Proficiency Test

The criteria under C-I/DEC.65 stipulates that a designated laboratory maintins a quality system in accordance with International Organization for Standardization/International Electrotechnical Commission (ISO/IEC) 17025:2005 standards and participates in the annual proficiency-testing to maintain a rating of three As or two As and one B in consecutive tests. Evalution of a laboratory's performance is based on the number of correctly identified chemicals minus misidentified chemicals to generate a performance rating (Table 1).

Table 1. Method of Evaluating Laboratory Performance[1]

| Performance Criteria Fulfilled | Identification of Chemicals | Performance Scoring | Performance Rating |
|---|---|---|---|
| Yes | Laboratory identifies all chemicals | Maximum score | A |
| Yes | Laboratory identifies all chemicals except one | Maximum score minus two | B |
| Yes | Laboratory identifies more than half of the chemicals | Score between zero and maximum minus two | C |
| Yes | Laboratory misses more chemicals than it identifies | Negative score | D |
| No | | No score | Failure |

1.2 Lewisite Structure and Hydrolyzed Products

L is a mixture of *cis* and *trans* isomers that are formed from the mixture of arsenic trichloride and acetylene. The structure of the different isomers and compounds that form L are shown in Figure 1. Physical chemical properties are listed in Table 2.

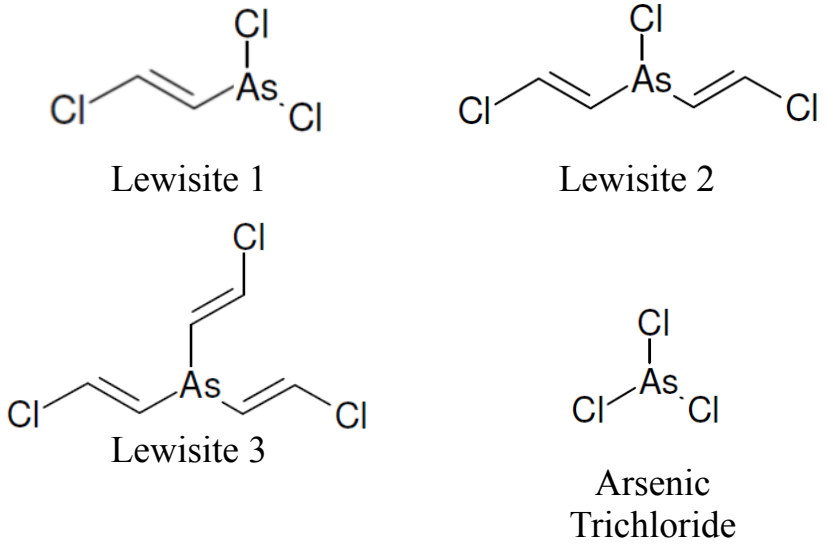


Figure 1. Structure of L-1, L-2, L-3, and precursor arsenic trichloride.

Table 2. Arsenic Containing CWA Compounds and Precursors Used in This Study[2]

| Compounds | Chemical Name | Structure | Molecular Weight | Percent Weight Arsenic |
|---|---|---|---|---|
| Lewisite 1 | 2-chlorovinylarsonous dichloride | $AsCl_3C_2H_2$ | 207.27 | 36.15% |
| Lewisite 2 | Bis(2-chlorovinyl) arsinous chloride | $AsCl_3C_4H_4$ | 233.27 | 32.12% |
| Lewisite 3 | Tris(2-chlrovinyl) arsine | $AsCl_3C_6H_6$ | 259.27 | 28.90% |
| Arsenic Trichloride | Arsenic Trichloride | $AsCl_3$ | 181.27 | 41.33% |

## 2. INSTRUMENTATION

### 2.1 Inductively Coupled Plasma-Mass Spectrometry

An Agilent Technologies (Santa Clara, CA) 7500cx series inductively coupled plasma-mass spectrometry (ICP-MS) equipped with a CETAC Technologies (Omaha, NE) ASX500 autosampler was used for the method development and sample analysis. ChemStation Version B.03.06 (Agilent Technologies, Santa Clara, CA) 2007 software was used to process the data.

### 2.2 Self Aspiration Mode

The data was collected with the nebulizer running in self aspiration mode. It was found that using a nebulizer in self aspiration mode reduced the signal noise.

### 2.3 Interferrents

Based on previous proficiency tests, the unknown samples are commonly in an organic solvent of hexane or dichloromethane[3]. When the sample is prepared for ICP-MS analysis, there is a trace level of organic solvent present. When diluting the sample in 3% nitric acid solution for ICP-MS analysis, if 250 µL of an unknown organic sample in pure solvent is diluted with 9.75 mL of 3% nitric acid, then 2.5% of the organic solvent will be in the autosampler vial. It is critical that all solutions analyzed with this sample contain the same percentage of the identical organic solvent. The process of aspirating the sample into the nebulizer and spray chamber for aerosolization is affected by the sample matrix. If the calibration standards do not have the same matrix of solvent and acid the arsenic levels detected may be inaccurate. All calibration curves were prepared with the same level of organic solvent as found in the test samples.

## 3. MATERIALS AND METHODS

Liquid argon, helium, and hydrogen gases were used in the collision and reaction chamber of the ICP-MS. All water was ultrapure 18 MΩ or double distilled water free of metals. High purity, distilled concentrated nitric acid ($HNO_3$), with minimum trace metals suitable for the intended detection level were purchased from VWR International, LLC (Radnor, PA). Agilent tuning solutions with 1 µg/L (ppb) and 10 µg/L (ppb) cerium, cobalt, lithium, thalium, and yttrium were used to verify the performance of the instrument at the start of each day.

All chemicals used for this report and their corresponding Chemical Abstracts Service (CAS) numbers are presented in Table 3. Solutions of the arsenic compounds were prepared by dissolving the neat standard in the corresponding organic solvent of hexane or dichloromethane in a glass volumetric flask. These "stock" solutions were then used to create the calibration standards and the "unknowns" for ICP-MS analysis. Stock solutions were made from Inorganic Ventures (Christiansburg, VA) ICP-MS standards. Table 4 outlines the preparation for the diluted stock solution created from the purchased stock solutions. Once all arsenic solution concentrations were adjusted, organic solvent was added to provide equal concentration in all samples and standards.

Table 3. Chemical Names and Corresponding CAS Numbers for the Chemicals Used

| **Chemical Name** | **CAS Number** |
|---|---|
| Argon | 7440-37-1 |
| Arsenic | 7440-38-2 |
| Arsenic Trichloride | 7784-34-1 |
| Cerium | 7440-45-1 |
| Cobalt | 7440-48-4 |
| Dichloromethane | 75-09-2 |
| Hexane | 110-54-3 |
| Lewisite 1 | 541-25-3 |
| Lewisite 2 | 40334-69-8 |
| Lewisite 3 | 40334-70-1 |
| Lithium | 7439-93-2 |
| Nitric Acid | 7697-37-2 |
| Thallium | 7440-28-0 |
| Water | 7732-18-5 |
| Yttrium | 7440-65-5 |

Table 4. Nominal Concentrations of Arsenic Calibration Standards, ppb = µg/L

| Stock Concentration of Arsenic (ppb) | Stock Volume (mL) | Final Volume (mL) | Concentration of Arsenic (ppb) |
|---|---|---|---|
| 1.00E+06 | 0.1000 | 100.0 | 1000.0 |
| 1000 | 0.2500 | 50.00 | 5.000 |
| 1000 | 0.5000 | 50.00 | 10.00 |
| 1000 | 1.250 | 50.00 | 25.00 |
| 1000 | 2.500 | 50.00 | 50.00 |
| 1000 | 5.000 | 50.00 | 100.0 |
| 1000 | 12.50 | 50.00 | 250.0 |
| 1000 | 25.00 | 50.00 | 500.0 |
| 1000 | 37.50 | 50.00 | 750.0 |
| 1000 | 50.00 | 50.00 | 1000.0 |
| 1000 | 25.00 | 50.00 | 500.0 |
| 1000 | 0.000 | 50.00 | 0.000 |

## 4. RESULTS

### 4.1 Calibration Curve Range

Arsenic solutions prepared in dichloromethane and hexane were prepared at $1.0x10^6$ ppb level. The samples were serially diluted as described above with 3% nitric acid. A range of calibration solutions were prepared from 0 to 1000 ppb.

At low levels, the measured values were 5% different from the expected values.

This was true for both interferrants shown in Figure 2. Figure 3 shows the full calibration range from 0 to 1000 ppb for each solvent.

Quantitative analysis of arsenic in solution was performed using a minimum of a five-point calibration curve and forcing the intercept through zero. Equation 1 was used to convert the signal into a concentration using the slope and intercept of the calibration curve

$$Y = \frac{(A/S)-B}{M} \quad (1)$$

where Y is the measured concentration (ppb), A is the signal of the analyte, S is the signal of the standard, B is the y-intercept, and M is the slope of the calibration curve. The measured concentration was converted to a final concentration by multiplying by a dilution factor

$$C_f = C_M \times (V_f/V_s) \quad (2)$$

where $C_f$ is the final concentration (ppb), $C_M$ is the measured concentration (ppb), $V_f$ is the final volume of the solution analyzed, and $V_s$ is the volume of the sample.

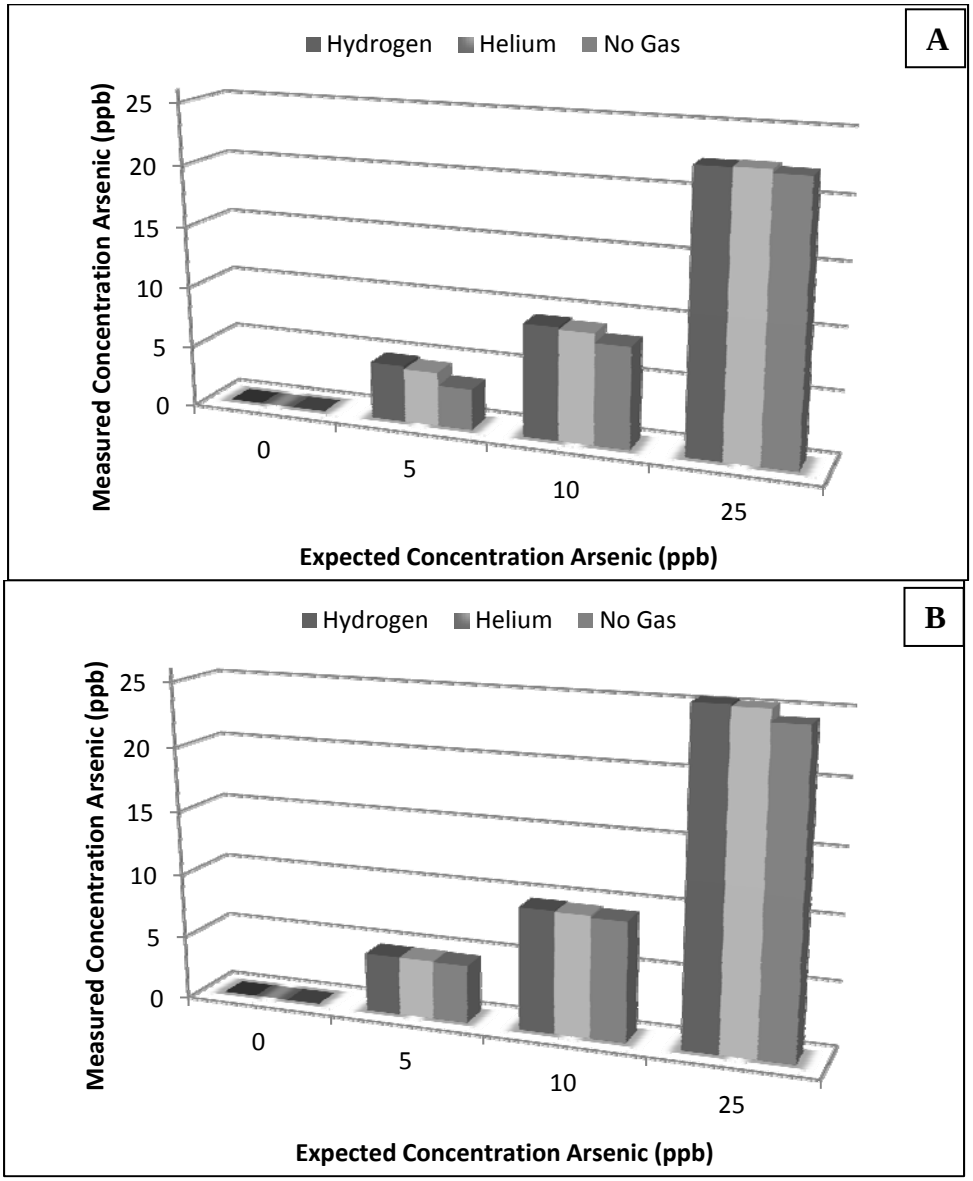


Figure 2. Day one calibration curves for arsenic from 0 to 25 ppb showing the variability in the three modes of detection at low levels in the presence of (A) dichloromethane and (B) hexane.

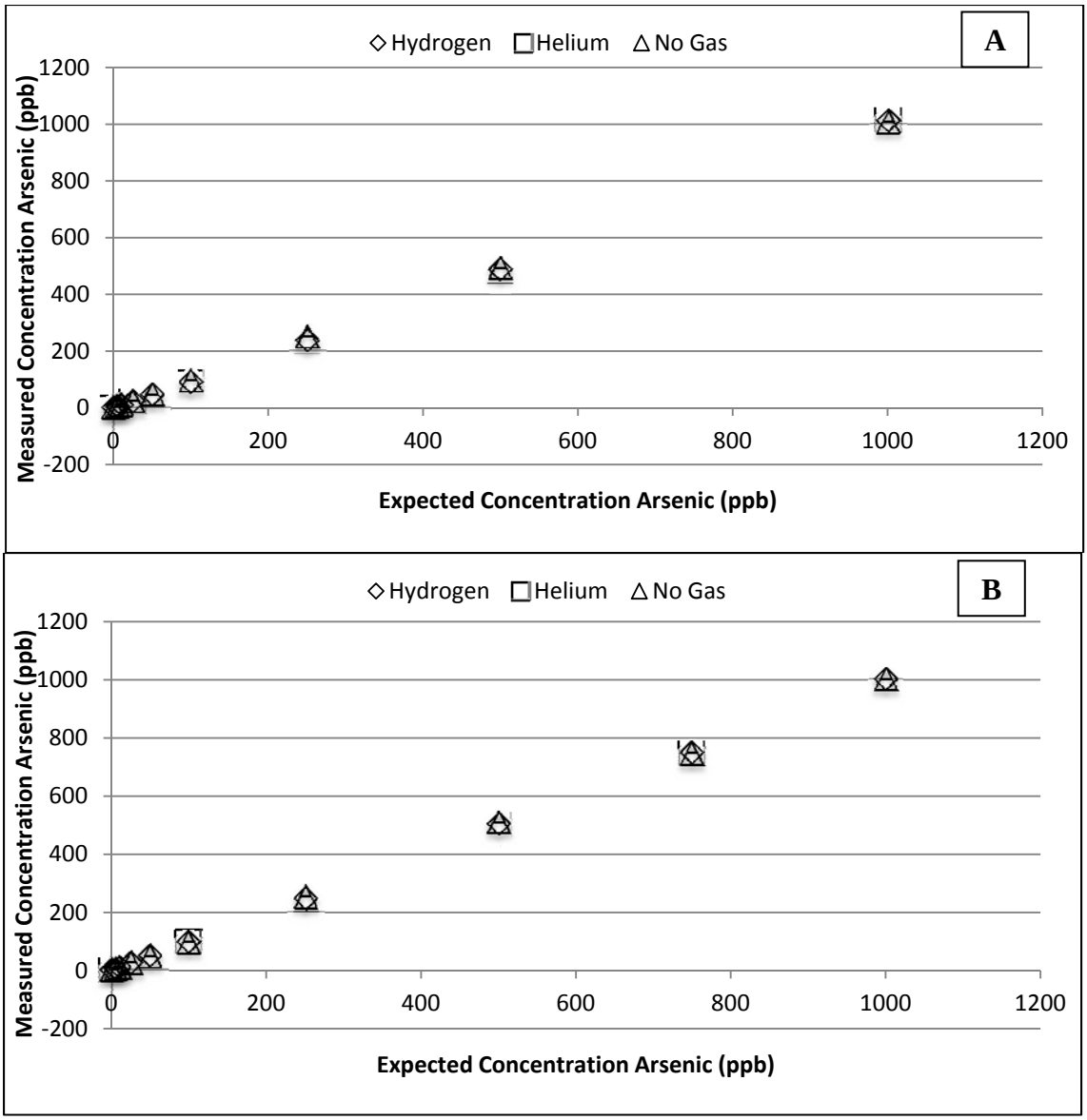


Figure 3. Calibration levels from 0 to1000 ppb for the three modes of analysis with (A) dichloromethane and (B) hexane as interferents.

## 4.2 Linearity

An eight point calibration curve was generated using dichlormethane as the trace organic and a nine point calibration curve for hexane as the trace organic. A minimum of six points should be used for daily calibrations. The calibration curves were linear for performance and analysis studies (P&As) and measurement of uncertainty studies with hexane and dichloromethane (Table 5).

Table 5. Linearity Measurements for P&A Day 1, Day 2 and Method Detection Limits (MDL)

| Analyte | Curve Type | Coefficient of Determination ($r^2$) | | |
|---|---|---|---|---|
| | | External Standard Mode | | |
| | | MDL | P&A Day 1 | P&A Day 2 |
| Mode:Hydrogen Solvent: Dichloromethane | Linear | 0.9986 | 0.9996 | 0.9986 |
| Mode:Hydrogen Solvent: Hexane | Linear | 0.9996 | 1.0000 | 0.9996 |
| Mode:Helium Solvent: Dichloromethane | Linear | 0.9990 | 0.9992 | 0.9990 |
| Mode:Helium Solvent: Hexane | Linear | 0.9976 | 1.0000 | 0.9976 |
| Mode:No Gas Solvent: Dichloromethane | Linear | 1.0000 | 1.0000 | 1.0000 |
| Mode:No Gas Solvent: Hexane | Linear | 0.9998 | 0.9998 | 0.9998 |

4.3 Performance and Analysis Studies (P&A)

The method reproducibility was conducted over two days using six solutions at each calibration level. A different analyst prepared the solutions on each day to capture the variability of the analyst. The same stock solution was used to prepare the solutions so the error was from the dilutions and pipette technique of the analyst. Tables 6 through 11 show the different solvents under the different gas conditions in the collision cell.

The precision of the samples was analyzed by calculating the relative percent difference (RPD) between the measured and expected concentrations

$$\left( \frac{C_M - C_E}{\text{Average } (C_M + C_E)} \right) \times 100\% \tag{3}$$

where $C_M$ is the concentration measured by the instrument and $C_E$ is the expected concentration. RPDs were less than 25% for the calibration standards at the levels presented in Tables 6 through 11.

Table 6. ICP-MS Data for the Arsenic P&A Study. "No Gas" Mode with Dichloromethane

| | Recovered Concentrations (µg/L) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **Level** | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** |
| **Spiked Conc. (µg/L)** | **5.000** | **10.00** | **25.00** | **50.00** | **100.0** | **250.0** | **500.0** | **750.0** | **1000.0** |
| **Replicate 1** | 4.049 | 9.766 | 25.10 | 51.08 | 110.6 | 274.3 | 525.8 | 800.6 | 1054 |
| **Replicate 2** | 3.974 | 9.744 | 24.50 | 54.48 | 109.2 | 273.6 | 520.1 | 818.2 | 1067 |
| **Replicate 3** | 4.052 | 9.248 | 24.99 | 50.92 | 115.6 | 274.1 | 545.2 | 795.6 | 1086 |
| **Replicate 4** | 5.327 | 10.11 | 26.26 | 51.49 | 106.5 | 256.8 | 511.8 | 784.9 | 1046 |
| **Replicate 5** | 5.232 | 9.642 | 24.26 | 47.67 | 105.3 | 262.6 | 511.5 | 736.3 | 995.8 |
| **Replicate 6** | 5.557 | 10.51 | 25.64 | 49.40 | 108.0 | 251.2 | 504.1 | 756.1 | 1002 |
| ***Mean Value:*** | 4.699 | 9.837 | 25.13 | 50.84 | 109.2 | 265.4 | 519.8 | 781.9 | 1042 |
| ***Mean % Recovery:*** | 93.97% | 98.37% | 100.5% | 101.7% | 109.2% | 106.2% | 104.0% | 104.3% | 104.2% |
| ***Standard Deviation:*** | 0.7458 | 0.4304 | 0.7364 | 2.274 | 3.657 | 10.06 | 14.56 | 30.36 | 35.93 |
| ***%RSD:*** | 15.87% | 4.375% | 2.931% | 4.473% | 3.349% | 3.788% | 2.802% | 3.883% | 3.449% |

RSD, relative standard deviation

Table 7. ICP-MS Data for the Arsenic P&A Study. Helium Mode with Dichloromethane

| | **Recovered Concentrations (µg/L)** | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **Level** | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** |
| **Spiked Conc. (µg/L)** | **5.000** | **10.00** | **25.00** | **50.00** | **100.0** | **250.0** | **500.0** | **750.0** | **1000.0** |
| **Replicate 1** | 5.394 | 11.34 | 25.63 | 57.82 | 107.3 | 278.8 | 544.5 | 831.9 | 1074 |
| **Replicate 2** | 5.609 | 11.19 | 26.08 | 52.58 | 105.0 | 267.2 | 526.1 | 816.4 | 1081 |
| **Replicate 3** | 5.255 | 10.79 | 27.01 | 56.66 | 110.9 | 271.5 | 541.1 | 819.3 | 1050 |
| **Replicate 4** | 5.444 | 10.48 | 25.72 | 49.67 | 98.39 | 251.0 | 516.5 | 787.2 | 1061 |
| **Replicate 5** | 6.124 | 10.94 | 26.49 | 53.02 | 100.5 | 265.1 | 508.8 | 797.5 | 1066 |
| **Replicate 6** | 5.806 | 11.38 | 27.70 | 53.15 | 104.7 | 256.5 | 523.9 | 802.0 | 1054 |
| ***Mean Value:*** | 5.605 | 11.02 | 26.44 | 53.82 | 104.5 | 265.0 | 526.8 | 809.1 | 1064 |
| ***Mean % Recovery:*** | 112.1% | 110.2% | 105.8% | 107.6% | 104.5% | 106.0% | 105.4% | 107.9% | 106.4% |
| ***Standard Deviation:*** | 0.3171 | 0.3498 | 0.8024 | 2.964 | 4.526 | 10.06 | 13.83 | 16.38 | 11.81 |
| ***%RSD:*** | 5.657% | 3.174% | 3.035% | 5.507% | 4.332% | 3.795% | 2.626% | 2.025% | 1.110% |

Table 8. ICP-MS Data for the Arsenic P&A Study. Hydrogen Mode with Dichloromethane

| | **Recovered Concentrations (µg/L)** | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **Level** | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** |
| **Spiked Conc. (µg/L)** | **5.000** | **10.00** | **25.00** | **50.00** | **100.0** | **250.0** | **500.0** | **750.0** | **1000.0** |
| **Replicate 1** | 5.979 | 12.15 | 27.00 | 55.92 | 107.5 | 261.9 | 540.8 | 791.6 | 1063 |
| **Replicate 2** | 6.116 | 12.04 | 27.61 | 55.70 | 106.4 | 271.7 | 529.4 | 823.8 | 1128 |
| **Replicate 3** | 5.939 | 11.93 | 28.46 | 54.33 | 108.6 | 269.8 | 540.2 | 828.5 | 1090 |
| **Replicate 4** | 5.539 | 10.75 | 25.65 | 50.72 | 101.3 | 255.6 | 531.5 | 816.1 | 1053 |
| **Replicate 5** | 6.242 | 11.17 | 26.61 | 50.48 | 102.9 | 262.1 | 509.1 | 801.4 | 1087 |
| **Replicate 6** | 5.928 | 11.86 | 28.77 | 53.38 | 104.6 | 261.3 | 523.7 | 827.1 | 1045 |
| ***Mean Value:*** | 5.957 | 11.650 | 27.35 | 53.42 | 105.2 | 263.7 | 529.1 | 814.8 | 1078 |
| ***Mean % Recovery:*** | 119.1% | 116.5% | 109.4% | 106.8% | 105.2% | 105.5% | 105.8% | 108.6% | 107.8% |
| ***Standard Deviation:*** | 0.2379 | 0.5595 | 1.173 | 2.375 | 2.798 | 5.973 | 11.79 | 15.10 | 30.54 |
| ***%RSD:*** | 3.990% | 4.802% | 4.288% | 4.446% | 2.659% | 2.265% | 2.228% | 1.853% | 2.834% |

Table 9. ICP-MS Data for the Arsenic P&A Study. "No Gas" Mode with Hexane

| | **Recovered Concentrations (µg/L)** | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **Level** | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** |
| **Spiked Conc. (µg/L)** | **5.000** | **10.00** | **25.00** | **50.00** | **100.0** | **250.0** | **500.0** | **750.0** | **1000.0** |
| **Replicate 1** | 4.709 | 9.676 | 25.84 | 49.71 | 99.65 | 266.0 | 525.0 | 763.6 | 1001 |
| **Replicate 2** | 4.895 | 9.954 | 25.65 | 50.89 | 101.1 | 272.4 | 540.8 | 797.2 | 1043 |
| **Replicate 3** | 5.230 | 10.30 | 26.22 | 51.94 | 102.3 | 272.2 | 538.6 | 772.1 | 1047 |
| **Replicate 4** | 4.173 | 9.617 | 24.66 | 47.62 | 91.88 | 224.9 | 497.8 | 734.3 | 996.7 |
| **Replicate 5** | 4.385 | 8.817 | 24.03 | 46.39 | 97.14 | 221.0 | 495.4 | 743.4 | 972.1 |
| **Replicate 6** | 4.590 | 9.041 | 24.15 | 46.49 | 92.65 | 220.9 | 494.0 | 762.2 | 976.4 |
| ***Mean Value:*** | 4.664 | 9.568 | 25.09 | 48.84 | 97.45 | 246.2 | 515.3 | 762.1 | 1006 |
| ***Mean % Recovery:*** | 93.27% | 95.68% | 100.4% | 97.68% | 97.45% | 98.49% | 103.1% | 101.6% | 100.6% |
| ***Standard Deviation:*** | 0.3742 | 0.5551 | 0.9322 | 2.349 | 4.378 | 26.39 | 22.11 | 22.17 | 32.21 |
| ***%RSD:*** | 8.024% | 5.802% | 3.715% | 4.809% | 4.493% | 10.719% | 4.290% | 2.908% | 3.202% |

Table 10. ICP-MS Data for the Arsenic P&A Study. Helium Mode with Hexane

| | Recovered Concentrations (µg/L) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **Level** | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** |
| **Spiked Conc. (µg/L)** | **5.000** | **10.00** | **25.00** | **50.00** | **100.0** | **250.0** | **500.0** | **750.0** | **1000.0** |
| **Replicate 1** | 4.869 | 10.02 | 27.06 | 51.88 | 104.8 | 261.6 | 519.5 | 768.7 | 1016 |
| **Replicate 2** | 5.091 | 10.30 | 26.90 | 53.43 | 106.2 | 265.8 | 541.9 | 800.3 | 1116 |
| **Replicate 3** | 5.478 | 10.77 | 27.50 | 54.83 | 107.7 | 268.4 | 534.7 | 776.6 | 1133 |
| **Replicate 4** | 4.398 | 9.907 | 25.37 | 49.10 | 96.71 | 215.3 | 486.3 | 729.0 | 1054 |
| **Replicate 5** | 4.597 | 9.232 | 25.24 | 48.45 | 99.77 | 212.9 | 488.0 | 738.6 | 1041 |
| **Replicate 6** | 4.814 | 9.378 | 25.02 | 49.04 | 97.20 | 213.9 | 484.1 | 741.9 | 1045 |
| ***Mean Value:*** | 4.875 | 9.935 | 26.18 | 51.12 | 102.1 | 239.7 | 509.1 | 759.2 | 1068 |
| ***Mean % Recovery:*** | 97.49% | 99.35% | 104.7% | 102.2% | 102.1% | 95.86% | 101.8% | 101.2% | 106.8% |
| ***Standard Deviation:*** | 0.3792 | 0.5732 | 1.0882 | 2.654 | 4.774 | 28.16 | 26.19 | 27.27 | 46.23 |
| ***%RSD:*** | 7.779% | 5.770% | 4.156% | 5.191% | 4.677% | 11.75% | 5.144% | 3.592% | 4.331% |

Table 11. ICP-MS Data for the Arsenic P&A Study. Hydrogen Mode with Hexane

| | **Recovered Concentrations (µg/L)** | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **Level** | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** |
| **Spiked Conc. (µg/L)** | **5.000** | **10.00** | **25.00** | **50.00** | **100.0** | **250.0** | **500.0** | **750.0** | **1000.0** |
| **Replicate 1** | 4.762 | 9.940 | 26.73 | 51.42 | 104.3 | 259.6 | 518.0 | 766.5 | 1004 |
| **Replicate 2** | 5.051 | 10.21 | 26.67 | 52.85 | 104.7 | 264.5 | 535.9 | 793.8 | 1047 |
| **Replicate 3** | 5.673 | 10.61 | 27.18 | 54.48 | 106.5 | 266.3 | 530.3 | 774.4 | 1053 |
| **Replicate 4** | 4.838 | 10.64 | 26.78 | 52.00 | 105.2 | 228.1 | 528.7 | 790.7 | 1048 |
| **Replicate 5** | 4.997 | 10.06 | 27.30 | 52.63 | 105.4 | 228.7 | 528.9 | 802.1 | 1051 |
| **Replicate 6** | 5.337 | 10.00 | 26.61 | 53.29 | 105.4 | 232.5 | 527.1 | 789.4 | 1058 |
| ***Mean Value:*** | 5.110 | 10.24 | 26.88 | 52.78 | 105.3 | 246.6 | 528.2 | 786.2 | 1044 |
| ***Mean % Recovery:*** | 102.2% | 102.4% | 107.5% | 105.6% | 105.3% | 98.65% | 105.6% | 104.8% | 104.4% |
| ***Standard Deviation:*** | 0.3405 | 0.3091 | 0.2884 | 1.062 | 0.7503 | 18.65 | 5.825 | 13.18 | 19.75 |
| ***%RSD:*** | 6.665% | 3.018% | 1.073% | 2.012% | 0.7129% | 7.562% | 1.103% | 1.676% | 1.892% |

4.4 Measurement of Uncertainty

Tables 12 and 13 show the performance quantitation limits (PQL) and the calculated measurements of uncertainty in the two day reproducibility test of the performance and analysis of six samples at each calibration level. Some levels of uncertainty were higher than expected. This is important for the treaty samples where the identification of a sample must be as precise and accurate as possible. Performing this analysis with the two trace level solvents as interferrants shows the importance of including this in the matrix of the calibration standards.

Table 12. Measurement Uncertainty Three Modes with Dichloromethane

| Analyte | Concentration (mg/L) | Uncertainty |
|---|---|---|
| **Arsenic (No Gas)** | 5.000 | 452 |
| | 10.00 | 226 |
| | 25.00* | 90 |
| | 50.00 | 47 |
| | 100.0 | 5.0 |
| | 250.0 | 14 |
| | 500.0 | 9.0 |
| | 1000.0 | 10.0 |
| **Arsenic (Helium)** | 5.000 | 429 |
| | 10.00 | 214 |
| | 25.00* | 86 |
| | 50.00 | 46 |
| | 100.0 | 24 |
| | 250.0 | 14 |
| | 500.0 | 8.0 |
| | 1000.0 | 4.0 |
| **Arsenic (Hydrogen )** | 5.000 | 447 |
| | 10.00 | 224 |
| | 25.00* | 90.0 |
| | 50.00 | 46 |
| | 100.0 | 23 |
| | 250.0 | 11 |
| | 500.0 | 8.0 |
| | 1000.0 | 8.0 |

* Denotes PQL identified through P&A, and measurement uncertainty (MU).

Table 13. Measurement Uncertainty Three Modes with Hexane

| Analyte | Concentration (mg/L) | Uncertainty (%) |
|---|---|---|
| **Arsenic (No Gas)** | 5.000 | 179 |
| | 10.00* | 90.0 |
| | 25.00 | 37 |
| | 50.00 | 21 |
| | 100.0 | 14 |
| | 250.0 | 27 |
| | 500.0 | 11 |
| | 750.0 | 8.0 |
| | 1000.0 | 8.0 |
| **Arsenic (Helium)** | 5.000 | 546 |
| | 10.00 | 273 |
| | 25.00 | 109 |
| | 50.00* | 6.0 |
| | 100.0 | 30.0 |
| | 250.0 | 31 |
| | 500.0 | 15 |
| | 750.0 | 10.0 |
| | 1000.0 | 12 |
| **Arsenic (Hydrogen )** | 5.000 | 227 |
| | 10.00 | 114 |
| | 25.00* | 45 |
| | 50.00 | 23 |
| | 100.0 | 11 |
| | 250.0 | 20.0 |
| | 500.0 | 4.0 |
| | 750.0 | 5.0 |
| | 1000.0 | 5.0 |

* Denotes PQL identified through P&A, and MU.

## 4.5 Analysis of Unknown Samples

Table 14 shows the representative samples used to simulate unknown treaty samples. Samples of L were prepared in dichloromethane and hexane representative of previous samples received. These unknowns were analyzed against calibration curves with the solvent to determine the level of accuracy in the reporting of the compound for identification purposes.

Table 14. Measurement of Unknown Arsenic Solution with and without Calibration with Interfering Solvent

| Analyte | Expected $[AsCl_3]$ ppm | Expected [As] ppm | Measured [As] ppb | | | Percent Recovery | | |
|---|---|---|---|---|---|---|---|---|
| | | | $H_2$ Mode | Helium Mode | No Gas Mode | $H_2$ Mode | Helium Mode | No Gas Mode |
| **$AsCl_3$** | 5.000 | 20.67 | 19.92 | 19.77 | 18.59 | 96.39 | 95.67 | 89.96 |
| **$AsCl_3$** | 50.00 | 206.6 | 173.3 | 166.7 | 152.1 | 83.86 | 80.67 | 73.60 |
| **2009 OPCW Sample** | 20.00 | 8.260 | 7.496 | 7.355 | 6.804 | 90.75 | 89.04 | 82.37 |

## 5. IMPLICATIONS FOR FUTURE APPLICATIONS

The ICP-MS in hydrogen mode has a high percent recovery when detecting arsenic in real world samples. Helium is the recommended mode to measure arsenic $^{75}As$ to distinguish m/z 75 from polyatomic interference by argon chloride $^{40}Ar^{35}Cl$ m/z 75 in the no gas mode[5]. Either hydrogen or helium appear to be sufficient at distinguishing arsenic in simulated treaty samples. Addition of 0.250 mL of solvent in the calibration standards significantly improved the detection of arsenic in samples with solvent. Arsenic levels measured 0 ppb without the solvent in the calibration standards and arsenic recoveries of 90% or better were detected with the solvent present. This simplified correction for detecting arsenic in samples avoids the tedious process of derivitization needed for gas chromatography-mass spectrometry (GC-MS), and allows for a quick screening technique in time sensitive samples. Increased sensisitivity of detection and speciation can be achieved with an optional oxygen line and hyphenated techniques such as the addition of an IC or high-performance liquid chromatography (HPLC) to the front end of the ICP-MS for chromatographic separation of the different arsenic species[6]. For the purposes of rapidly screening samples for presence and absence this method was validated and found to have detection levels suitable for screening OPCW samples.

LITERATURE CITED


1. *Standard Operating Procedure for the Organisation of OPCW Proficiency Tests, Rev 2, Issue 2*, QDOC/LAB/SOP/PT01; Organisation for the Prohibition of Chemical Weapons: The Hague, The Netherlands, 2012.

2. *Recommended Operating Procedures for Analysis in the Verification of Chemical Disarmament;* Vanninenm P., Ed.; The Ministry for Foreign Affairs of Finland: University of Helsinki, 2011.

3 *Evaluation of Results Twenty-Fifth Official OPCW Proficiency Test*; Organisation for the Prohibition of Chemical Weapons: The Hague, The Netherlands, 2009.

4. Organisation for the Prohibition of Chemical Weapons - Basic Facts on Chemical Disarmament. < http://www.opcw.org/news-publications/publications/history-of-the-chemical-weapons-convention/#c4135> (accessed November 23, 2012).

5 Getting the Most from What You've Got: How to Improve Data Quality with Any ICP-MS. ICP-MS Training, provided November 4, 2011 at University of Maryland, Baltimore County. Thermo Fisher Scientific: Waltham, MA.

6 Raber, G.; Raml, R.; Goessler, W.; Francesconi, K.A. Quantitative Speciation of Arsenic Compounds when Using Organic Solvent Gradients in HPLC-MS. *J. Anal. At. Spectrom.* **2010**, *25*, 570-576.

# BIBLIOGRAPHY

*Agilent 7500 Series ICP-MS Chem Station Operator Manual, Rev A.* G3270-90115; Agilent Technologies: Santa Clara, CA, September 2007.

*Agilent 7500 Series ICP-MS Customer Maintenance Parts List, Rev A.* G3270-90124; Agilent Technologies: Santa Clara, CA, April 2007.

*Agilent 7500 Series ICP-MS Hardware Manual*, *Rev C.* G3270-90104; Agilent Technologies: Santa Clara, CA, October 2007.

*Agilent 7500 Series ICP-MS Installation Guide, Rev B.* G3270-90213; Agilent Technologies: Santa Clara, CA, June 2007.

*Agilent 7500 Series ICP-MS Option Instruction Manual*, *Rev C*. G3270-90140; Agilent Technologies: Santa Clara, CA, April 2007.

*Agilent 7500 Series ICP-MS Maintenance Video (DVD), Rev A.* G3270-65100; Agilent Technologies: Santa Clara, CA, September 2005.

*Agilent ASX-500 Series Autosampler (CD Rev A.* G3286-90200; Agilent Technologies, CA, March 2006.

Environmental Protection Agency, 2007. *Method 6020A, Revision 1, Inductively Coupled Plasma-Mass Spectrometry*. <www.epa.gov/osw/hazard/testmethods/sw846/pdfs/6020a.pdf>

ACRONYMS AND ABBREVIATIONS

| | |
|---|---|
| CAS | Chemical Abstract Service |
| CVAA | chlorovinyl arsonous acid |
| CWA | chemical warfare agents |
| ECBC | U.S. Army Edgewood Chemical Biological Center |
| FAC | Forensic Analytical Center |
| GC-MS | gas chromatography-mass spectrometry |
| HPLC | high-performance liquid chromatography |
| ICP-MS | inductively coupled plasma-mass spectrometry |
| ISO/IEC | International Organization for Standardization/International Electrotechnical Commission |
| L | lewisite |
| MDL | method detection limit |
| MU | measurement uncertainty |
| OPCW | Organization for the Prohibition of Chemical Weapons |
| P&A | performance and analysis |
| PQL | performance quantitation limits |
| RPD | relative percent difference |
| RSD | relative standard deviation |


EDGEWOOD CHEMICAL BIOLOGICAL CENTER
A U.S. Army RDECOM Laboratory